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(54) Detergent formulations.

(57) This invention relates to aqueous based liquid detergent formulations comprising a homogeneous dispersion of water, surfactants, builder salts and a clay. The clay is pretreated with a barrier material such as a polysiloxane prior to incorporation in the formulation. These formulations have viscosity stability and good freeze-thaw stability. The formulations also impart softness to the fabrics washed therewith.

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DETERGENT FORMULATIONS

The present invention relates to liquid detergent formulations containing clay as a component. Most liquid detergent formulations are aqueous based. Conventionally these formulations have primarily performed the function of cleansing the fabrics washed whereas the softening of the washed fabric has been performed by a separate formulation introduced usually during the rinse cycle of the wash.

More recently, attempts have been made to devise liquid formulations which perform both functions in a single formulation. One such formulation has attempted the use of the conventional non-ionic silicone surfactants. However these silicone surfactants do not impart any softness to the fabric. Moreover, these formulations may result in instability; the silicone component may cause phase separation of the formulation, especially during freeze-thaw cycling.

Another set of well known fabric softening agents are the tetra-alkyl quaternary ammonium halides, especially the di(hydrogenated tallow)- and distearyl-dialkyl ammonium halides. However, these are cationic softeners and are not compatible with liquid detergents which contain an anionic component.

A further set of compounds which is believed to have a softening effect on fabrics are clays, especially the smectite type clays. Several recent publications, notably GB-A-2201172, GB-A-1400898, GB-A-1462484, GB-A-2132629 and EP 225142 describe the use of smectite type clays in various formulations. However, these clays are well known for their ability to increase in volume by several fold and to form a gelatinous/thixotropic substance when in contact with water. Since, in general, liquid detergent formulations are aqueous based and may already contain suspended solids, this results in considerable changes in viscosity of the formulation upon storage for any length of time. Due to the fact that clays are known to be less efficient softeners than quaternary ammonium salts, relatively large quantites of clay have to be used to achieve desirable levels of softness and this in turn exacerbates the problems of viscosity variations in such formulations.

It has now been found that two of the conventional softeners, which are relatively inefficient or give rise to effects such as increased viscosity and phase separation when used individually in liquids, show an unexpectedly high softening effect and good viscosity stability when used in combination without adversely affecting the cleansing efficiency of the formulation.

Accordingly, the present invention is an aqueous based liquid detergent formulation comprising in a homogenous dispersion or suspension water, one or more surfactants, a builder salt and a clay characterised in that the clay is pretreated with one or more barrier materials selected from a siloxane, a polysiloxane, a polyacrylate, dialkyl citrate, alkoxylated dialkyl citrate, alkoxylated glycerol mono- and distearates, and alkoxylated N-alkyl alkanolamides prior to incorporation of the clay in the formulation.

By the expression "barrier material" as used herein and throughout the specification is meant one or more materials listed herein whenever used to pretreat a clay by coating, impregnating or otherwise having incorporated therein or on the surface thereof one or more of the materials listed whether or not such treatment results in the material acting as a protective barrier on the clay so treated.

Any of the well known surfactants can be used in the detergent compositions of the present invention. A typical list of these surfactants can be found in EP-A-225142 and in EP-A-11340.

Examples of water soluble anionic surfactants include the salts of alkyl benzene sulphonates and paraffin sulphonates. Similarly, salts of alkyl sulphates, alkyl polyalkoxy ether sulphates, fatty acid monoglyceride sulphates and sulphonates and alkyl phenol polyalkoxy ether sulphates may also be used.

Suitable examples of the above surfactants are linear straight chain alkyl benzene sulphonates having alkyl groups with 8-16 carbon atoms and methyl branched alkyl sulphates having 8-16 carbon atoms which are also effective.

Other anionic detergent compounds suitable for use herein include the sodium fatty acid monoglyceride sulphonates and sulphates derived from coconut oil; and sodium or porassium salts of C_8-C_{12} alkyl phenol alkylene oxide ether sulphate containing up to 10 alkylene oxide units per molecule. Mixtures of anionic surfactants may also be used. A substantial list of such compounds can be found in e.g. McCutcheon's Dictionary of Emulsifiers and Detergents, International Edition (1981), published by the Manufacturing Confectioner Publishing Co. and in "Surfactants Europa: A Directory of Surface Active Agents available in Europe", Ed. Gordon L. Hollis, Vol 1 (1982), published by George Goodwin.

Th nonionic surfactants which may be used in the present invention are condensates of an alkylene oxide e.g. ethylene oxide with a hydrophobic group to form a surfactant having an appropriate hydrophilic-lipophilic balance (HLB) in the range from 8 to 17, suitably from 9.5 to 13.5, preferably from 10 to 12.5. The hydrophobic group may be an aliphatic or aromatic type and the length of the polyoxyethylene group condensed therewith can be readily adjusted to yield a water-soluble compound having the desired degree

of HLB.

Examples of suitable nonionic surfactants include:

(a) The polyethylene oxide condensates of alkyl phenol in which the alkyl group e.g. contains from 6 to 12 carbon atoms and in which from 3 to 30 moles, preferably 3 to 14 moles of ethylene oxide are present. Other examples include a mole of dodecylphenol condensed with 6 moles of ethylene oxide, a mole of dinonylphenol condensed with 9 moles of ethylene oxide and a mole of nonylphenol and octadecylphenol condensed with 11 moles of ethylene oxide.

(b) The nonionic surfactant may also be formed as a condensation product of a mole of primary or secondary C_8-C_{16} aliphatic alcohols with from 2 to 30 moles, preferably 2 to 9 moles of ethylene oxide.

Specific examples of nonionic surfactants useful for the purposes of the invention include the various grades of Dobanol (Registered Trade Mark, supplied by Shell) Lutensol (Registered Trade Mark, supplied by BASF) and Synperonics (Registered Trade Mark, supplied by ICI).

The amount of surfactant in the formulation is suitably from 2-30% w/w, preferably from 6-15% w/w of the total formulation.

An essential component of detergent compositions in accordance with the invention is one or more detergent builder salts which may comprise up to 35% of the composition, more typically from 5 to 25% by weight thereof. Suitable detergent builder salts useful herein can be of the polyvalent inorganic and polyvalent organic types or mixtures thereof. Examples of suitable water-soluble, inorganic alkaline detergent builder salts include the alkali metal carbonates, phosphates, pyrophosphates, tripolyphosphates and bicarbonates.

Examples of suitable organic alkaline detergency builder salts are water-soluble polycarboxylates such as the salts of nitrilotriacetic acid, lactic acid, glycollic acid and ether derivatives thereof; succinic acid, malonic acid, (ethylenedioxy)diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid; citric acid, aconitic acid, citraconic acid, carboxymethyloxysuccinic acid, lactoxysuccinic acid, and 2-oxy-1,1,3-propane tricarboxylic acid; oxydisuccinic acid, 1,1,2,2-ethane tetracarboxylic acid, 1,1,3,3-propane tetracarboxylic acid and 1,1,2,3-propane tetracarboxylic acid; cyclopentane-cis, cis,cis-tetracarboxylic acid, cyclopentadiene pentacarboxylic acid, 2,3,4,5-tetrahydrofuran-cis, cis, cis-tetracarboxylic acid, 2,3,4,5-tetrahydrofuran-cis, cis, cis-tetracarboxylic acid, 2,5-tetrahydrofuran-cis-dicarboxylic acid, 1,2,3,4,5,6-hexanehexacarboxylic acid, mellitic acid, pyromellitic acid and the phthalic acid derivatives.

Water-insoluble detergent builders can also be used. A specific example of such builders are the zeolites especially the sodium type A zeolite typified by SASIL (Registered Trade Mark).

Mixtures of organic and/or inorganic builders can also be used.

Particularly preferred as builder salts are the alkali metal pyrophosphates and alkali metal tripolyphosphates.

The builder salts are suitably present in an amount from 1-35% w/w, preferably from 5-25% w/w based on the total formulation. In some cases it may be necessary to add buffering agents in order to control the pH value of the formulation within the desired range. Buffering agents of this type will be well known to those skilled in the art. Examples include a combination of borax and glycerol.

The feature of the invention is the use of a clay component which has been pretreated with a barrier material prior to incorporation in the detergent formulation.

As clays may be used any aluminosilicate type material which has the ability to impart softening to fabrics laundered with a formulation containing the same. Clays having an ion-exchange capacity of at least 50 meq/100g of clay (milliequivalents per 100g of clay) are preferred. Specific examples of such clays include smectite type clays. These latter clays are multi-layered clays which layered structure is capable of increasing the volume thereof several-fold by their ability to swell or expand when in contact with water and thereby form a thixotropic gelatinious substance.

Such clays are well known in the art and are described for example in GB-A-2201172, GB-A-1400898, GB-A-1462484, GB-A-2132629 and EP-A-225142 which are incorporated herein by reference. Specific examples of clays that may be used in the present invention include bentonite, montmorillonite, nontronite, volchonskite, saponite, hectorite, sanconite and vermiculite, and mixtures thereof.

The clays used may be hydrophilic or organophilic provided that pre-treatment thereof with the barrier materials is carried out prior to incorporation in the detergent formulation.

The barrier material used is one or more of siloxanes, polyacrylates, dialkyl citrate, alkoxylated dialkyl citrate, alkoxylated glycerol mono- and distearates, and alkoxylated N-alkyl alkanolamides. Of these siloxanes are preferred.

The polysiloxanes used to treat the clays have the gen ral formula:

$$(R_6)_3Si[OSi(R_7)_2]_m[OSiR_8]_p[OSiR_9]_q[OSiR_{10}]_rOSi(R_6)_3 \qquad (I)$$

$$\qquad\qquad\qquad\qquad\qquad\quad |\qquad\quad |\qquad\quad |$$

$$\qquad\qquad\qquad\qquad\qquad\quad R_1\qquad R_2\qquad H$$

wherein R_1, R_6, R_7, R_8 R_9 and R_{10} are the same or different groups of the formula $(CH_2)_tCH_3$,
R_2 = $-(CH_2)_z(OCH_2.CHR_3)_x(OCH_2CHR_4)_y-OR_5$
in which each of R_3 and R_4 are H or a $-CH_3$ group such that the resultant polyoxyalkylene derivative is a polymer of ethylene oxide and/or a random or block copolymer of ethylene oxide and propylene oxide,
R_5 = H, a C_1-C_4 alkyl or an acetoxy group,
x = 1-50
y = 0-40
z = 1-10
t = 0-21
m = 0-1000
p = 0-100
q = 1-50 and
r = 0-10

The siloxanes (I) used as barrier materials are derivable by the reaction of a siloxane with an olefin and excess alkylene oxide. However, the product of this reaction may be used directly as the barrier material even though such a product may be a mixture of (I) and some unreacted or partially reacted materials. In such a product the siloxane (I) is the predominant component. Thus, for instance, if the reaction of all -OSi-(H)(R_{10})- groups in the siloxane with the alkylene oxide is complete, the value of r can be 0 in formula (I) because this will represent the absence of any unreacted -OSi(R_{10})(H)- groups in the siloxane used.

In compounds of the formula (I), the preferred siloxanes have the following values for the various notations used:-
m = 5-120
p = 0-40
q = 1-15
r = 0-5
x = 5-15
y = 1-10
z = 2-5
R_1 = $(CH_2)_tCH_3$ where t = 9-19,
R_3 is H
R_4 = R_6 = R_7 = R_8 = R_9 = R_{10} = $-CH_3$, and
R_5 is H or $-CH_3$

The amount of clay present in the formulation is suitably from 1 to 50%, preferably from 2 to 30% by weight of the total formulation.

The clay may be, for instance, pre-treated with the barrier material by any one of the following methods. For example it may be spray coated neat or from a suitable solvent, coated from eg. a fluidised bed, dry-milled or by admixture of clay, barrier material and a solvent followed by evaporation of the solvent.

By using the treatment methods referred to above the clay may be coated, impregnated or otherwise have incorporated therein or on the surface thereof some or all of the barrier material used for the treatment. For instance, if a siloxane is used as the barrier material and the incorporation of the material onto clay is from a solution of the siloxane, on the clay suitably has from 0.1 to 50%w/w, preferably from 1 to 30% w/w of the polysiloxane based on the total treated clay.

The detergent formulation is a liquid. The formulations can be a heavy duty type liquid detergent (HDLD) and the detergent formulation can be formed by thoroughly mixing the treated clay with the other ingredients of the detergent using a high speed mixer.

The amount of treat d clay pres nt in the detergent formulation is suitably that which is sufficient to maintain the desired viscosity without loss of stability.

The detergent formulations disclosed herein can contain other materials commonly us d in such compositions. For example, various soil-suspending agents such as carboxymethyl-cellulose, corrosion inhibitors, dyes, optical brightners, suds-boosters, suds-depressants, germicides, anti-tarnishing agents such as sodium silicate, and enzymes, well known in the art for use in detergent formulations can also be

employed herein. Bound water can also be present in said detergent formulations.

The detergent formulations of the present invention can be prepared in several ways. For instance, a portion of the builder salt can initially be added to water before additon of the pre-treated clay and the surfactant. Such a method gives a homogeneousdispersion having uniform rheological properties. Also, it is possible to add the necessary amount of water at a temperature of e.g. 40-50° C to a mixer provided with a stirrer; thereafter between 25 and 5% of the builder salt is added thereto with stirring; the pre-treated clay is then added and formed into a homogeneous dispersion with stirring and the mixture is then cooled.

The formulations of the present invention initially have a viscosity of less than 3000 CPS, preferably less than 1500 CPS at 20° C and more preferably lie in the range of 600-1000CPS, and a shear rate of 21 Sec^{-1}. Viscosities below 600 CPS can result in loss of stability.

The treated clays used in the formulations of the present invention not only give softness to the fabric washed therewith but also have the effect of maintaining the stability of the formulation. The fabrics so treated can also facilitate ironing of the washed fabrics.

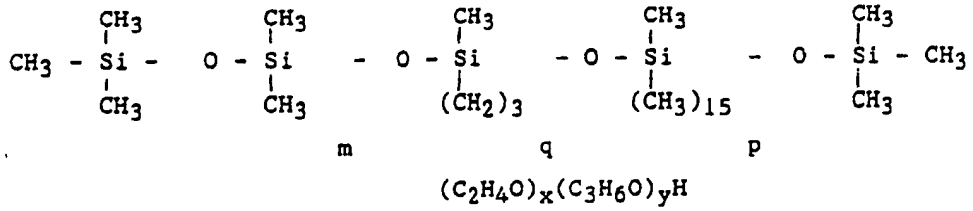
The present invention is further illustrated with reference to the following Examples.

1. Clays

The clay tested in these Examples was Texas bentonite clay.

2. Barrier Material Tested

2.1 Siloxane, Product Y



Product Y mwt = 13,600 m = 40, q = 13, p = 0
x = 12, y = 3, a water soluble siloxane polyether

3. Performance Testing

3.1 Siloxanes Alone

(a) On Cloth Surface

To assess whether the siloxane would confer softening when present on the cloth surface, the siloxane was deposited onto cloth as a 1% solution in chloroform. After drying at room temperature for several hours, the treated cloths (400gsm terry towelling) was assessed for softness by a small test panel, against a cloth treated by the solvent only, and ranked. Product Y gave good softening.

(b) Incorporation of Product Y into Wisk * Liquid

*Wisk is a registered trade Mark and is a commercial liquid detergent ex Unilever

To simulate washing machine conditions, cloths were treated in a beaker at typical Wisk concentrations (eg. 10g/l) at 60°C. After drying and conditioning for 24 hours at 20°C and 60% relative humidity, the cloths were ranked for softness by panel assessment.

Results showed that Wisk liquid plus 1% Product Y gave no improvement in softness compared with treatment with Wisk alone.

(c) Stability

Wisk was stable to a 0.5% inclusion of Pruduct Y. A 1% level of Product Y caused phase separation when mixed directly into Wisk liquid or when formulated into a typical Wisk-type structured liquid detergent formulation.

3.2 Clay Alone

(a) Softening

A screening test on terry towelling treated with Wisk plus 5 and 10% levels of Texas bentonite clay showed better softening than by treatment with Wisk alone as judged by a test panel. However, softening did not approach that obtained by washing in Bold 3 (a commercial powdered detergent/softener ex Procter and Gamble).

(b) Viscosity and Stability

The viscosity of Wisk was approximately 740 cP at a shear rate of $20s^{-1}$ at 25°C.
Wisk + 5% clay = 1140 cP
Wisk + 10% clay = 1410 cP
Wisk plus 10% clay exhibited phase separation after one freeze-thaw cycle; Wisk plus 5% clay separated after two cycles.

3.3 Conclusion

It appeared that, although siloxanes conferred softening when they reached and adhered to the cloth surface, they could not do so in the presence of a typical Wisk-type heavy duty liquid detergent (HDLD). Incorporation of 1% of Product Y also reduced the viscosity of Wisk, resulting in phase separation.

Incorporation of clay resulted in an increase in viscosity and instability to freeze-thaw cycling.

4. Clays Coated With Siloxanes

Due to the thickening caused by clay addition and the thinning and instability caused by Product Y addition to a Wisk-type HDLD, it was decided to coat the clay with Product Y in an attempt to overcome both undesirable effects. It also provided a delivery system to enable the softening properties of Product Y to be transferred to the fabric surface.

4.1 Coating of Product Y onto clay - Clay Pre-treatment

The initial method of coating was designed to give a surface coating of siloxane on sodium montmorillonite. For a 10% by weight coating, 20g siloxane was dissolved (or dispersed) in approximately 200 cm^3 chloroform and 180 g Texas b ntonite clay was added. The solv nt was evaporated, followed by oven drying of the clay for 2 hours at 70°C. Any lumps of clay were ground to a fine powder.

4.2 Softness

Initial Softness Screening in Wash Liquor

In this screening test method 10% of the coated clay was added to the Wisk liquid prior to the test wash.

The results from this trial (10% clay coated with 10% siloxane i.e. 1% siloxane as a percentage of final formulation) appear conclusive. Numbers correspond to softness ranking of treatment i.e. 1 means softest cloth, 3 means harshest assessed.

Panellist	Wisk	Bold 3	Wisk + clay Product Y
A	3	2	1
B	3	2	1
C	3	2	1
D	3	2	1
E	3	2	1
Total Rank	15	10	5

Panel Softness Test Using Dummy Bundles

Four realistic wash loads (2.5 Kg of 50:50 cotton/synthetic), each containing 5 test pieces were treated in a wash cycle (20L water) with:-

1. 200g Wisk
2. 200g Bold 3
3. 200g Asda HDLD & fabric conditioner detergent (a commercial liquid detergent containing a fabric conditioning clay additive).

200g Wisk plus 10% clay/Product Y (10% incorporation onto clay)

Test pieces were hang dried at 20° and 60% RH. The results of an internal panel test are shown in full (1 = ranked best ,4 = worst)

Panellist	Wisk	Bold 3	ASDA Liquid	Wisk + Clay/Product Y
A	4	1	3	2
B	4	1	3	2
C	4	2	3	1
D	4	3	2	1
E	4	2	3	1
Total Rank	20	9	14	7

Wisk plus clay/Product Y appears to outperform both the currently used powders and liquid detergents combined with fabric conditioners. The increased softening due to both siloxane and clay at the cloth surface came from a pre-treated clay according to the invention.

4.3 Viscosity and Stability

Effect of Incorporation on Stability and Viscosity of Wisk Liquid

Level of Clay Coated with Product Y	Initial Visc	After 6 days at 20°C
5% clay/10% Y	793	1090
10% clay/10% Y	825	1100
5% clay/20% Y	910	1100
10% clay/20% Y	650	960

The 10% clay:Product Y samples survived 6 freeze-thaw cycles. 5% clay samples were stable to at least 15 freeze-thaw cycles.

The coating with product Y therefore enables a softening clay to be incorporated into Wisk liquid whilst maintaining freeze-thaw stability.

Claims

1. An aqueous based liquid detergent formulation comprising in a homogeneous dispersion or suspension water, one or more surfactants, a builder salt and a clay characterised in that the clay is pretreated with one or more of the barrier materials selected from a siloxane, a polysiloxane, a polyacrylate, dialkyl citrate, alkoxylated dialkyl citrate, alkoxylated glycerol mono- and di-stearates, and alkoxylated N-alkyl alkanolamides prior to incorporation of the clay in the formulation.

2. A formulation according to Claim 1 wherein the clay is pretreated with the barrier material by coating, impregnating or otherwise having incorporated therein or on the surface thereof one or more of the barrier materials.

3. A formulation according to Claim 1 or 2 wherein the clay is an aluminosilicate having an ion-exchange capacity of at least 50 meq/100g of clay.

4. A formulation according to Claim 3 wherein the clay is a smectite type clay.

5. A formulation according to any one of the preceding Claims wherein the clay is selected from bentonite, montmorillonite, nontronite, volchonskite, saponite, hectorite, sanconite, vermiculite and mixtures thereof.

6. A formulation according to any one of the preceding Claims wherein the clay is present in the formulation in an amount from 1 to 50%w/w.

7. A formulation according to any one of the preceding Claims wherein the barrier material is a polysiloxane of the general formula.

$$(R_6)_3Si[OSi(R_7)_2]_m[OSiR_6]_p[OSiR_9]_q[OSiR_{10}]_rOSi(R_6)_3$$

$$\begin{array}{ccc} | & | & | \\ R_1 & R_2 & H \end{array}$$

wherein R_1, R_6, R_7, R_8, R_9 and R_{10} are the same or different groups of the formula $(CH_2)_tCH_3$,
$r_2 = -CH_2)_z(OCH_2.CHR_3)_x(OCH_2CHR_4)y\text{-}OR_5$
in which each of R_3 and R_4 are H or a $-CH_3$ group such that the resultant polyoxalkylene derivative is a polymer of ethylene oxide and propylene oxide,
R_5 = H, a C_1-C_4 alkyl or an acetoxy group,
x = 1-50
y = 0-40
z = 1-10
t = 0-21
m = 0-1000
p = 0-100
q = 1-50 and
r = 0-10.

8. A formulation according to any one of the preceding Claims wherein the clay has from 0.1-50%w/w

of the barrier material based on the total treated clay.

9. A formulation according to any one of the preceding Claims wherein said formulation has an initial viscosity of less than 3000 CPS at 20° C and a shear rate of 21 sec^{-1}.

10. A formulation according to any one of the preceding Claims wherein the formulation is prepared by initally adding a builder salt to water before addition of the pre-treated clay and the surfactant.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 30 1039

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-291262 (UNILEVER) * page 2, lines 41 - 43; claims 1-5 *	1	C11D3/12
A	GB-A-2170235 (COLGATE-PALMOLIVE) * page 6, lines 24 - 37; claims 1-8 *	1	
A	US-A-4374939 (J. VAN FISK) * column 5, lines 4 - 23; claims 1-47 *	1	
A	FR-A-2541301 (COLGATE-PALMOLIVE) * claims 1-6 *	1	
A	EP-A-225142 (UNILEVER) * claim 9 *	10	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	11 MAY 1990	PFANNENSTEIN H.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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